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| Author(s)    | Islam, Md. Tarikul; Hossain, Mohammad Imran; Aoki, Kentaro; Nagao, Yuki; Hasan, Md. Mahmudul; Rahaman, Mostafizur; Aldalbahi, Ali; Hasnat, Mohammad A.                                                                                                                                                                                                                                                                                                                                                                                                                                   |
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# Electrochemical Reduction of CO<sub>2</sub> by SnS| PTFE| Pt Surface in an Aqueous Imidazole Medium: Catalysis and Kinetics

Md. Tarikul Islam <sup>a,1</sup>, Mohammad Imran Hossain <sup>a,1</sup>, Kentaro Aoki <sup>b</sup>, Yuki Nagao <sup>b</sup>, Md. Mahmudul Hasan <sup>c</sup>, Mostafizur Rahaman <sup>d</sup>, Ali Aldalbahi <sup>d</sup>, Mohammad A. Hasnat <sup>a\*</sup>

<sup>a</sup> *Electrochemistry & Catalysis Research Laboratory (ECRL), Department of Chemistry, School of Physical Sciences, Shahjalal University of Science and Technology, Sylhet-3114, Bangladesh*

<sup>b</sup> *School of Materials Science, Japan Advanced Institute of Science and Technology, 1-1 Asahidai, Nomi, Ishikawa, 923-1292, Japan*

<sup>c</sup> *Research Organization for Nano and Life Innovation, Waseda University, Shinjuku, Tokyo 162-0041, Japan*

<sup>d</sup> *Department of Chemistry, College of Science, King Saud University, P.O. Box 2455, Riyadh 11451, Saudi Arabia*

**\*Corresponding authors:**

Mohammad A. Hasnat, E-mail: [mah-che@sust.edu](mailto:mah-che@sust.edu)

<sup>1</sup> Both authors have equal contribution

## Abstract

Development of a novel SnS| PTFE| Pt electrode as an efficient catalyst for electrochemical CO<sub>2</sub> reduction to formate in aqueous alkaline imidazole medium is reported in this paper. The electrode was prepared through the incorporation of poly-tetrafluoroethylene (PTFE) with SnS and modification of Pt surface by SnS/PTFE. The electrode facilitated a first-order CO<sub>2</sub> reduction at -1.1 V vs. Ag/AgCl (saturated KCl) via a diffusion-controlled pathway with a cathodic electron transfer coefficient ( $\alpha$ ) of 0.22 and two-electron transfer kinetics in two steps, where the first electron transfer step determined the reaction rate. The SnS| PTFE| Pt electrode surface exhibited well-defined cyclic voltammograms (CVs) for CO<sub>2</sub> reduction in comparison to GCE, Au, Pd, and graphite-modified electrodes utilizing the same catalyst, indicating superior catalytic efficiency and its conduciveness to kinetic investigations. Such performance

indicates that the SnS| PTFE| Pt electrode would be a promising alternative for CO<sub>2</sub> reduction in the context of renewable energy generation.

**Keywords:** electrochemical CO<sub>2</sub> reduction, formate, kinetics, cyclic voltammetry, catalyst, renewable energy

## 1. Introduction

The emission of carbon dioxide (CO<sub>2</sub>) into the atmosphere has long been a serious concern to environmentalists as well as scientists. Due to the extensive utilization of fossil fuels, the level of CO<sub>2</sub> is increasing in the atmosphere resulting in an elevated global temperature. CO<sub>2</sub> has a unique linear structure comprised of different vibrational and rotational modes that can absorb different wavelengths; thus, it can retain the radiation from the Sun contributing to global warming. Alarmingly, CO<sub>2</sub> constitutes 76% of the total greenhouse gas emissions.<sup>1</sup> Consequently, researchers are incessantly trying to reduce CO<sub>2</sub> in the atmosphere by utilizing it as a renewable energy source and through the development of CO<sub>2</sub> capture and storage technologies.<sup>2,3</sup> In recent decades, various methods including electrochemical, photochemical, and photoelectrochemical have been employed to convert CO<sub>2</sub> into useful chemicals.<sup>4,5</sup> Among these, the electrochemical CO<sub>2</sub> reduction holds significant promise for energy conversion purposes, since it is easily scalable for large scale electricity production and can be conducted under ambient temperature and pressure conditions.

The stable linear geometry of CO<sub>2</sub> and the presence of high energy anti-bonding lowest unoccupied molecular orbitals (LUMO) result in a high energy barrier for single electron transfer during CO<sub>2</sub> reduction.<sup>6</sup> The metallic surface offers a way of activating this inert molecule for reduction reaction by adsorbing CO<sub>2</sub> on its surface and forming a partially negative species (CO<sub>2</sub><sup>δ-/-</sup>) through interaction with surface atoms.<sup>7</sup> Subsequently, the negative intermediate species undergoes further reduction to generate a stable product, the composition of which is dependent upon various factors including reaction conditions, electrolytes, and notably, the electrode materials employed.<sup>8,9</sup> Particularly, the conversion of CO<sub>2</sub> to non-toxic liquid like formate is highly desirable owing to its large market value. Formate compounds can further be subjected to application in direct fuel cells as hydrogen carrier systems.<sup>10</sup> The development of robust electrocatalysts for the selective conversion of CO<sub>2</sub> to formate by effectively surmounting the large energy barriers in CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) remains an ongoing area of global research interest.

Several reductive pathways leading to distinct oxidation states of carbon (from  $\text{C}_2\text{O}_4^{2-}$  to  $\text{CH}_4$ ) have been documented in the scientific literature.<sup>11–13</sup> Previous studies have shown that transition metal and p-block metal electrodes, such as Au, Ag, Cu, Pd, Pt, In, Sn, Hg, and Pb are attractive candidates for  $\text{CO}_2$  reduction reaction.<sup>14–16</sup> Among them, Cu is the only metal catalyst that was found to produce considerable C1–C3 hydrocarbon products.<sup>17</sup> Koper *et al.* reported that bimetallic Pd-Pt alloy nanoparticles exhibit a very low onset potential and a high Faradaic efficiency for the selective reduction of  $\text{CO}_2$  to  $\text{HCOOH}$ .<sup>18</sup> Au is the most active metal electro-catalyst for the reduction of  $\text{CO}_2$  to CO. However, the catalytic activity on Au is still limited by the high activation energy of  $\text{CO}_2$  during reduction.<sup>19</sup> In contrast, Pt provides favorable surface for activation and conversion of  $\text{CO}_2$  to adsorbed CO at low reaction temperature (limiting step is CO desorption).<sup>20,21</sup> Because of the facile activation of  $\text{CO}_2$  on Pt surfaces, it holds great potential as a substrate for the development of  $\text{CO}_2$ -based fuel cells through further modifications. In particular, non-precious p-block metals such as tin (Sn) are excellent candidates for electrocatalysis due to their low catalytic activity towards the competing hydrogen evolution reaction (HER) and high selectivity towards the production of formates during  $\text{CO}_2$  reduction reactions.<sup>22–25</sup> Consequently, there is a pressing need to design a bimetallic catalyst based on Pt and Sn that exhibits facile activation of  $\text{CO}_2$  and its subsequent conversion to harmless as well as profitable reaction products.

Facilitating multiple electron transfer reactions in  $\text{CO}_2$  reduction by stabilizing adsorbed gaseous species on the electrode surface presents a significant challenge. However, this challenge can be overcome by employing poly-tetrafluoroethene (PTFE), which acts as a porous polymer matrix that traps intermediate species, thus mitigating the issue.<sup>26,27</sup> The addition of PTFE to various metallic catalysts has been found to enhance their catalytic activity and increase Faradaic efficiency in  $\text{CO}_2$  reduction by elevating the concentration of intermediate products.<sup>28,29</sup>

An additional noteworthy obstacle in the  $\text{CO}_2$  reduction process is the difficulty in amassing a reaction medium with an adequate amount of  $\text{CO}_2$  gas. In this context, amine compounds have been recognized for their efficacy in adsorbing  $\text{CO}_2$  at room temperature and ambient pressure.<sup>30</sup> As such, an aqueous environment containing compounds that contain amine groups, such as imidazole ( $\text{C}_3\text{N}_2\text{H}_4$ ), is capable of capturing  $\text{CO}_2$  gas and delivering a suitable amount of  $\text{CO}_2$  to the surface of the electrode for reduction. In an aqueous environment, amino groups undergo protonation, leading to the formation of  $>\text{NH}_2^+$  groups. These  $>\text{NH}_2^+$  groups act as

Lewis acids and exhibit a strong interaction with CO<sub>2</sub>, which acts as a Lewis base. This interaction enhances the solubility of CO<sub>2</sub>.<sup>31</sup> The presence of active >NH<sub>2</sub><sup>+</sup> sites in the structure of imidazole enables improved catalytic performance during CO<sub>2</sub> reduction.<sup>32</sup>

Furthermore, the use of sulfur (S) modulated Sn nanomaterials has demonstrated remarkable efficacy in the selective and sensitive conversion of CO<sub>2</sub> to formic acid.<sup>33</sup> SnS modified electrodes were found to exhibit superior performance over electrodes modified with Sn nanoparticles.<sup>34</sup> This is attributed to the increased selectivity facilitated by S, as the presence of S favors the formation of thermodynamically favorable formate intermediates.<sup>35</sup> This study aims to design a stable and nanostructured SnS catalyst modified electrode by immobilizing SnS onto Pt surfaces with the assistance of PTFE. The catalytic performance kinetics for CO<sub>2</sub> reduction reaction will be investigated. To the best of our knowledge, no such kinetic study pertaining to electrochemical reduction reaction of CO<sub>2</sub> was reported in any previous literature.

## **2. Experimental**

### **2.1. Materials and Instruments**

Imidazole, sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), and PTFE (poly-tetrafluoroethene) solution were purchased from Sigma Aldrich, USA for carrying out this study. The pure CO<sub>2</sub> gas was obtained in high-pressure liquid form and stored in a cylinder for dissolution into an aqueous imidazole medium. Deionized water, with a resistivity of approximately 18 MΩ cm<sup>-1</sup>, was employed in the experiment. All the electrochemical experiments were performed employing Autolab potentiostat (PGSTST 128N, The Netherlands) and Wave Driver 10 (Pine Incorp., USA) in combination with the globally acknowledged three electrode system. A Pt electrode having an active geometric area of 0.0314 cm<sup>2</sup> protected with a Teflon layer had been used as the working electrode. Subsequent modification of the Pt electrode was carried out to fabricate the viable working electrode to attain CO<sub>2</sub>RR. In this study, a Pt wire was utilized as a counter electrode and a silver/silver chloride (Ag/AgCl) electrode, saturated with potassium chloride (KCl), was employed as the reference electrode. As such, all potentials cited in this article are presented with reference to the Ag/AgCl (saturated KCl) reference electrode. The product of CO<sub>2</sub> electroreduction was analyzed using a gas chromatograph-mass spectrometer (GC-MS) instrument (GCMS-QP2020 model manufactured by Shimadzu Corporation, Japan) by setting an oven temperature to 35 °C, injection temperature to 250 °C, and split ratio to 90:1. The GC-

MS analysis allowed for identification of the product based its retention time peak and mass spectrum.

## **2.2. Preparation of SnS Catalyst**

A standard procedure was followed for the synthesis of nanocrystalline SnS, wherein a stoichiometric ratio of 2:1 of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  and thiourea  $[\text{CS}(\text{NH}_2)_2]$  were dissolved in water and the resulting mixture was vigorously stirred for a duration of 2 hours. The resulting solution, following stirring, was transferred to a 200 mL Teflon-lined autoclave, with additional water added to occupy 80% of the total volume. The autoclave was subsequently heated to 200 °C for a period of 8 hours, within an electric furnace. Upon completion of the heating process, the autoclave was allowed to cool naturally to room temperature. The resulting brownish precipitate was collected via centrifugation and subjected to multiple washes using absolute ethanol and Milli-Q water. Finally, the product was dried in an open atmosphere, and in an oven within the temperature range of 50-60 °C for a period of 2 hours, before being used for modifying the pristine Pt electrode.

## **2.3. Modification of Pt Surface**

Initially, the surface of the Pt electrode was polished on a polishing pad following a pattern resembling the numeral 'eight (8)' utilizing alumina slurries consisting a particle size of around 0.3  $\mu\text{m}$  in diameter, until a smooth and shiny surface was achieved. The Pt electrode was subjected to ultrasonic treatment in the presence of 0.5 M  $\text{H}_2\text{SO}_4$  and acetone for a duration of 20 minutes at 25 °C. The addition of acetone to the treating solution facilitated the effective removal of any organic impurities that might have been adhered to the electrode surface after mechanical cleaning. Following the ultrasonic treatment, the Pt electrode was subsequently subjected to electrochemical cleaning employing a potentiostatic system. The electrode was cycled in a 0.1 M  $\text{H}_2\text{SO}_4$  electrolyte, sweeping potential between -0.2 V and 1.5 V vs. Ag/AgCl (saturated KCl) at scan rate of 100  $\text{mVs}^{-1}$  until a stable and reproducible cyclic voltammograms (CVs) corresponding to characteristics behavior of Pt were achieved. In the subsequent step, 1 mg of the synthesized SnS catalyst was dissolved in ethanol, and then subjected to ultrasonication to achieve a well-dispersed state of SnS particles. Following this, the sol medium was mixed with a 5% (w/w) solution of polytetrafluoroethylene (PTFE) to obtain a paste. A droplet of the paste was deposited onto the surface of the Pt electrode using a micro pipette, and the electrode was then heated at 80°C for 10 minutes in an oven to obtain a uniform

coating. Herein, PTFE was utilized as a non-conductive medium and binder, which provided a stabilizing layer for the mechanically deposited SnS nanoparticles.

## 2.4. Electrochemical Measurements

For potentiostatic measurements, a conventional 3-electrode system was assembled by employing the SnS| PTFE| Pt electrode as the working electrode, along with Ag/AgCl (saturated with KCl) reference and Pt counter electrodes. To elucidate the electronic properties of SnS| PTFE| Pt electrode, linear polarization curves were obtained in a 0.1 M imidazole solution under N<sub>2</sub> saturated condition, firstly in the absence of CO<sub>2</sub>, followed by in the presence of saturated CO<sub>2</sub> condition. Additionally, the electrochemical impedance was also determined for saturated CO<sub>2</sub> in 0.1 M imidazole by applying an excitation potential of -1.1 V vs. Ag/AgCl (saturated KCl) at SnS| PTFE| Pt electrode. Concentration effect was investigated by performing CV measurements after introducing CO<sub>2</sub> into 0.1 M imidazole solution through purging, where CO<sub>2</sub> concentration was ensured by measuring it quantitatively with the total organic content analyzer. Mass transfer effect was studied in potentiostatic mode at a saturated condition of CO<sub>2</sub> by altering the scan rate ranging from 0.05 to 0.5 Vs<sup>-1</sup>. Subsequently, linear sweep voltammograms (LSVs) were obtained for hydrodynamic analysis in saturated CO<sub>2</sub> in 0.1 M imidazole at varied rotation rates (100-900 rpm) employing the Modulated Speed Rotator (PINE, USA). To minimize any discrepancies in the experimental outcomes, inert conditions were maintained throughout the experiments employing N<sub>2</sub> gas.

## 2.5. Morphological and Chemical Characterization

The morphological characterization of the catalyst deposited mechanically on Pt electrode was performed by X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, powder X-ray diffraction (PXRD), energy dispersive X-ray (EDX), transmission electron microscopy (TEM), and field emission scanning electron microscopy (FESEM). At first, the prepared SnS catalyst was morphologically characterized using a field emission scanning electron microscope (FESEM), (JSM-7610F, Japan). PXRD patterns were recorded using a Rigaku SmartLAB diffractometer with Cu K $\alpha$  irradiation ( $\lambda = 1.5406 \text{ \AA}$ ). Le Bail fitting was carried out using TOPAS3 (Bruker AXS). TEM measurement was conducted using HITACHI H-7650 electron microscope with an acceleration voltage of 100 kV. EDX analysis was performed using the TM3030Plus miniscope (Hitachi Ltd.). To unravel the chemical states of SnS formed, binding energies were determined by analyzing the XPS spectra recorded with a delay-line detector

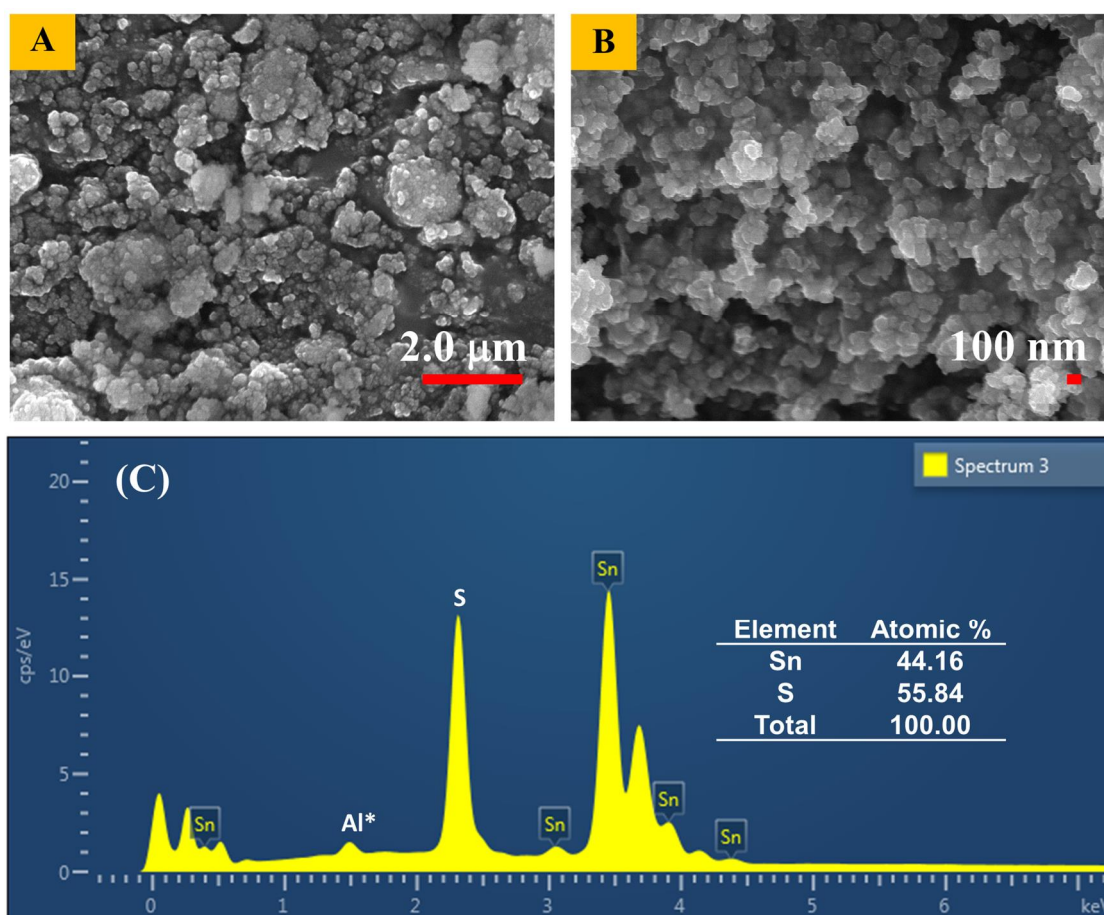
(DLD) spectrometer (Kratos Axis-Ultra; Kratos Analytical Ltd.) with an Al K $\alpha$  radiation source (1486.6 eV). Finally, to further confirm the successful synthesis of SnS, Raman spectra of SnS particles were recorded with Ava Raman spectrometer (785 nm laser: Avantes, Netherlands).

### **3. Results and Discussion**

#### **3.1. Characterization**

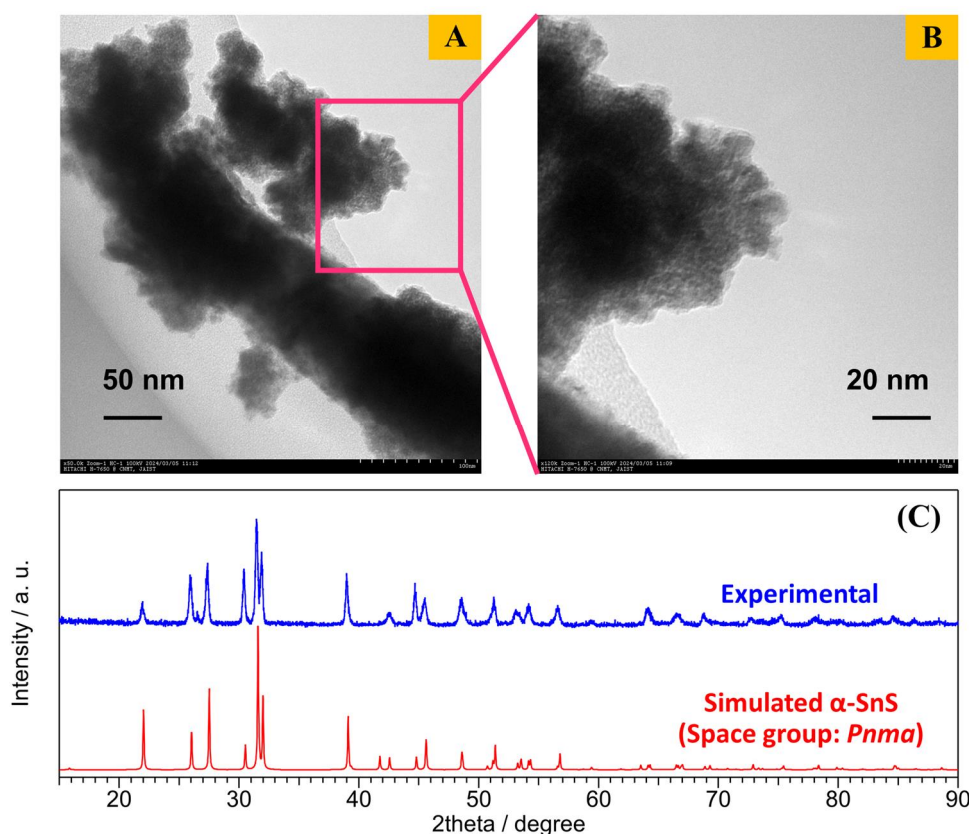
##### **3.1.1. Morphological and Elemental Analysis**

**Figure 1(A-B)** presents the field emission scanning electron microscope (FESEM) images of the as-synthesized SnS particles captured at two different magnifications. In **Figure 1(A)**, the dispersed SnS particles can be observed, wherein both individual particles and certain agglomerations can be discerned. **Figure 1(B)** reveals that SnS particles actually consist of clusters of nanoparticles having multiple inter-particle connections. **Figure 1(C)** shows the energy dispersive X-ray (EDX) spectrum of the SnS particles in **Figure 1(A-B)**. The Figure clearly demonstrates the successful synthesis of the intended SnS composition. The atomic % ratio of Sn to S was determined to be 1:1.3, suggesting the coexistence of Sn<sup>2+</sup> and Sn<sup>4+</sup> species.



**Figure 1.** SEM images of the synthesized SnS particles at (A) 22,000 and (B) 30,000 times magnifications. (C) EDX elemental spectrum of SnS particles (the peak for Al arose from the sample holder).

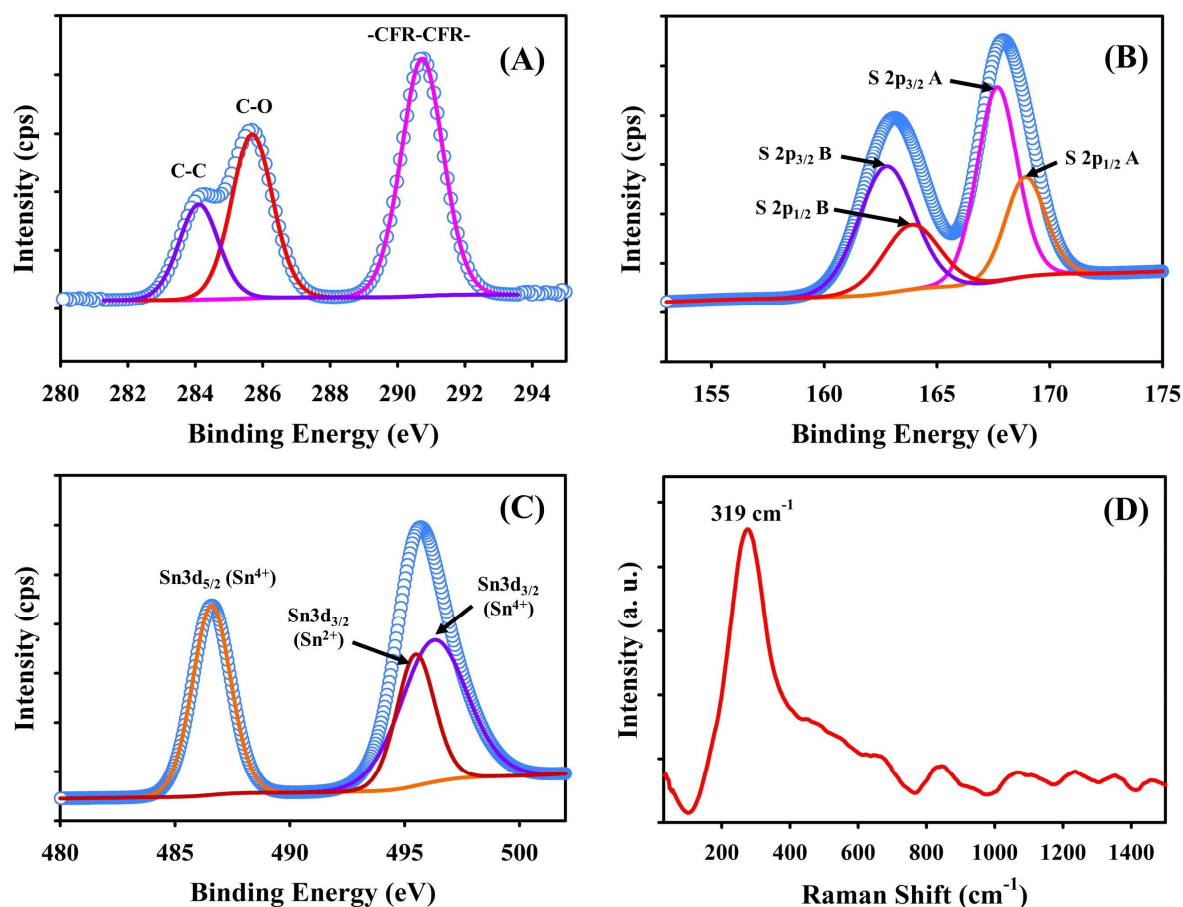
**Figure 2(A-B)** depicts the transmission electron microscope (TEM) images of SnS particles. In **Figure 2(A)**, a rod-shaped large particle and a smaller particle can be observed, both corresponding to SnS crystals. The large rod-like particle was assigned to divalent Sn component, as evidences by the powder X-ray diffraction (PXRD) data in **Figure 2(C)**. The smaller particle in **Figure 2(B)** might be attributed to the tetravalent species of Sn component.<sup>36,37</sup> The PXRD patterns of SnS crystalline particles depicted in **Figure 2(C)** correspond closely to the simulated  $\alpha$ -SnS phase, possessing a space group of  $Pnma$ .<sup>38</sup> No secondary phase or other impurities were observed. Structural parameters of synthesized SnS from PXRD analysis are stated in **Table S1** in the Supporting Information.



**Figure 2.** TEM images of SnS particles at (A) 50,000 and (B) 120,000 times magnification. (C) Comparison of PXRD patterns between the synthesized and simulated SnS particles.

**Figure 3(A-C)** presents the curve-fitted high resolution X-ray photoelectron spectra of the catalyst used to modify the Pt surface. **Figure 3(A)** exhibits the XPS spectra in the C1s region originating from PTFE. The prominent peak located at a binding energy of 290.8 eV is characteristics of  $-(CF_2-CF_2)_n-$  bonds which constitute the PTFE structure.<sup>39</sup> The other two carbon environments found are: carbon atoms of C–O bonds at 285.6 eV and carbon atoms of C–C bonds at 284.1 eV.<sup>40</sup> **Figure 3(B)** shows the XPS spectra of the electrode surface modifying catalyst in the S2p region. Binding energies at 163 eV and 164.13 eV corresponds S2p<sub>3/2</sub> and S2p<sub>1/2</sub> species, respectively.<sup>41</sup> A doublet separation of ~1.2 eV between the S2p peaks is a good typical value for metal sulfide. Interestingly, two more resolvable peaks around 167.8 eV and 169 eV is observed which corresponds to S2p<sub>3/2</sub> and S2p<sub>1/2</sub> species, respectively.<sup>41</sup> These two additional peaks serve as evidence for the presence of metal sulfide in the catalyst matrix.<sup>41</sup> **Figure 3(C)** presents the XPS spectra of the catalyst in Sn3d region. Components of Sn3d located at about 486.9 eV and 496.3 eV are ascribed to Sn3d<sub>5/2</sub> and Sn3d<sub>3/2</sub>, respectively.<sup>42,43</sup> A difference of approximately 9 eV between the two prominent peaks observed in the Sn3d region is indicative of the tetravalent Sn 3d states.<sup>41</sup> The observed binding

energies suggest the existence of SnS within the catalyst. Another noteworthy peak centered at 495.6 eV can be assigned to the Sn3d<sub>3/2</sub> associated with the Sn<sup>2+</sup> oxidation state present in SnS. Since Sn<sup>2+</sup> has a lower positive oxidation state compared to Sn<sup>4+</sup>, Sn3d<sub>3/2</sub> peak for Sn<sup>2+</sup> appeared at lower binding energy due to less coulombic interaction.<sup>42</sup> The catalyst was further characterized using Raman spectral analysis as shown in **Figure 3(D)**. The distinct peak observed at 319 cm<sup>-1</sup> is indicative of the A<sub>g</sub> mode of SnS nanoparticles.<sup>43–45</sup>

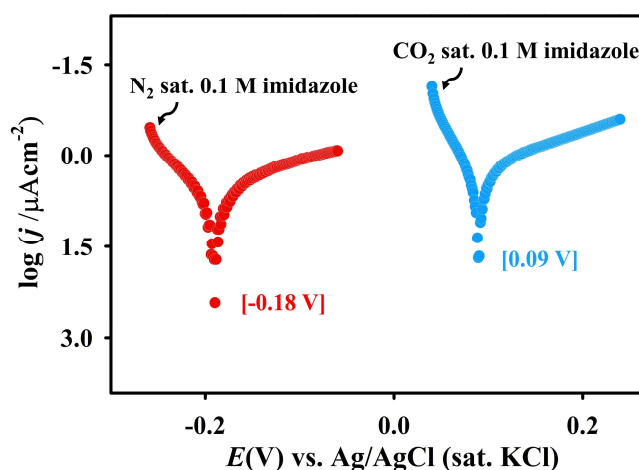


**Figure 3.** Morphology analysis of SnS| PTFE on electrode surface. XPS spectra of (A) C1s, (B) S2p, and (C) Sn3d of SnS/PTFE. (D) Raman spectra of SnS nanoparticles.

### 3.1.2. Electrochemical Characterization

The electrochemical characterization of SnS| PTFE| Pt electrode was performed by running a linear polarization where the potential at zero current is measured. **Figure 4** shows the linear polarization curves recorded by the SnS| PTFE| Pt electrode in absence and presence of CO<sub>2</sub> in 0.1 M imidazole solution. As the SnS| PTFE| Pt system was expected to be catalytically

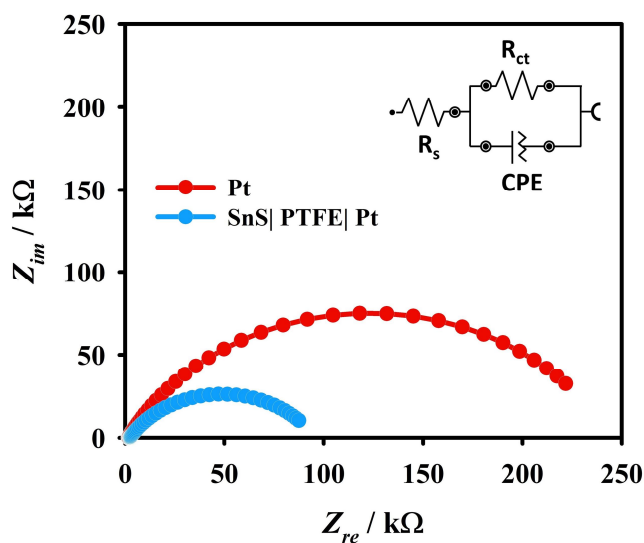
viable, the nature of electronic charge developed was assessed when nanoparticles in SnS| PTFE| Pt interface interact with CO<sub>2</sub> at open circuit condition in 0.1 M imidazole. In N<sub>2</sub> saturated condition, it can be observed from **Figure 4** that SnS| PTFE| Pt exhibited zero current at an open circuit potential (OCP) of -0.18 V vs. Ag/AgCl (saturated KCl) reference electrode. However, in presence of CO<sub>2</sub>, the OCP value displaced to a comparatively more positive value (0.09 V) which suggests an accumulation of positive charge on the electrode surface. The observed positive shift in the modified electrode's behavior can be attributed to the increased presence of positively charged  $\delta^-O-\delta^+C-O\delta^-$  molecules at the SnS| PTFE| Pt electrode. These molecules tend to withdraw electron density from the electrode's surface, resulting in a net positive charge on the surface. Moreover, it can be assumed from the OCP value that SnS| PTFE| Pt electrode may catalyze the CO<sub>2</sub> reduction at potentials below 0.09 V.



**Figure 4.** Linear polarization curves for the SnS| PTFE| Pt electrode in N<sub>2</sub> and CO<sub>2</sub> saturated 0.1 M imidazole solutions.

Next, to perceive the provable charge transfer properties of SnS nanoparticles immobilized on Pt surface, the electrochemical impedance spectra (EIS) of the electrodes were recorded in CO<sub>2</sub> saturated imidazole by applying a potential below OCP value e.g., -1.1 V as the excitation potential. The conventional Nyquist plots obtained using Pt and SnS| PTFE| Pt electrodes are shown in **Figure 5**. The polarization resistance ( $R_{ct}$ ) values for Pt surface and SnS| PTFE| Pt electrode were found 221.84 k $\Omega$  and 86.08 k $\Omega$ , respectively. The higher charge transfer resistance ( $R_{ct}$ ) observed on the Pt surface suggests a greater degree of polarizable character. In contrast, SnS| PTFE| Pt electrode exhibits a decreased polarizable character, leading to a lower charge transfer resistance compared to the bare Pt. This decrease in polarizable character

indicates the formation of catalytic sites on electrode surface, which are conducive to CO<sub>2</sub> reduction by this electrode.

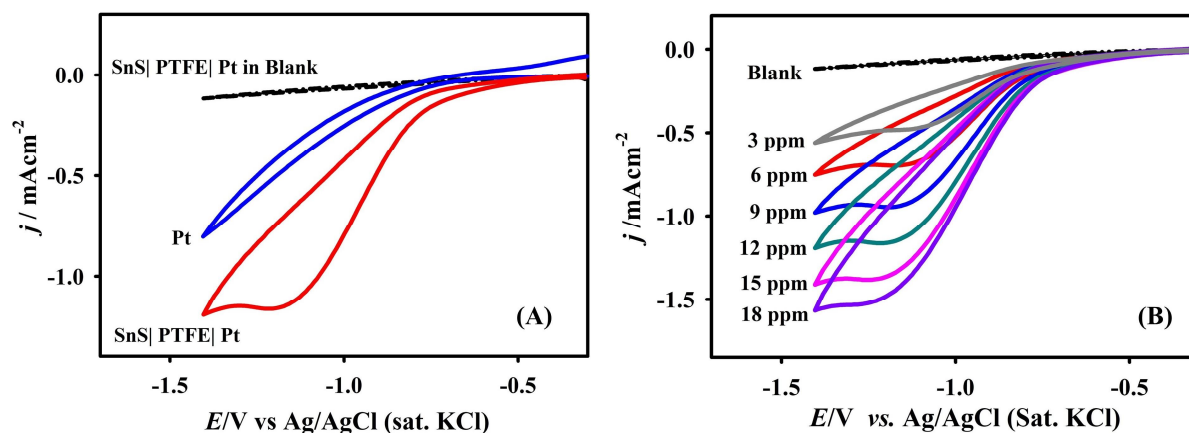


**Figure 5.** EIS spectra of CO<sub>2</sub> saturated 0.1 M imidazole solution recorded by applying -1.1 V vs. Ag/AgCl (saturated KCl) reference electrode as the excitation potential at Pt and SnS| PTFE| Pt electrodes.

### 3.2. Cyclic Voltammetry Analysis

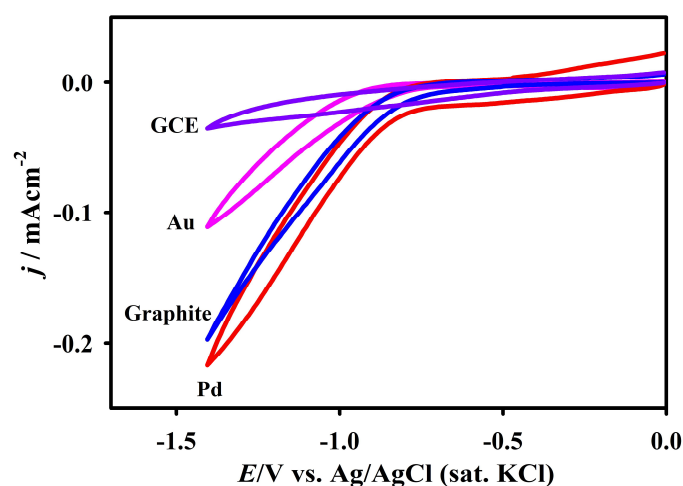
As outlined in previous section, the electrochemical impedance spectroscopic (EIS) examination revealed that the modified SnS| PTFE| Pt electrode potentially produces catalytic sites for CO<sub>2</sub> reduction. Consequently, to assess the catalytic performance, CV analysis was conducted on both Pt and SnS| PTFE| Pt electrodes using a CO<sub>2</sub>-saturated imidazole solution, employing a scan rate of 50 mVs<sup>-1</sup>. It is clearly seen from **Figure 6(A)** that while potential scanning was performed between -0.2 to -1.4 V vs. Ag/AgCl (saturated KCl), only SnS| PTFE| Pt electrode generated a diffusive current resulting from the reduction of CO<sub>2</sub>. In case of bare Pt electrode, potential dependent kinetic current was observed which implies that under the experimental condition, SnS| PTFE| Pt electrode possess more active catalytic sites than a pristine Pt electrode to execute CO<sub>2</sub> reduction. It is thus evident that when SnS nanoparticles are immobilized on the Pt surface, a robust catalytic effect is generated with an onset potential ( $E_i$ ) of -0.6 V vs. Ag/AgCl (saturated KCl), and a peak potential ( $E_p$ ) of -1.1 V vs. Ag/AgCl (saturated KCl). These observations indicate that SnS| PTFE| Pt can allow quicker electron transfer due to presence of SnS sites in the catalytic matrix. It is to be noted that no significant competition from the hydrogen evolution reaction was observed in the working

potential range as depicted by the dashed-line CV obtained at N<sub>2</sub> saturated blank imidazole solution in **Figure 6(A)**.



**Figure 6.** (A) Cyclic voltammograms (CVs) of CO<sub>2</sub> saturated 0.1 M imidazole solution acquired at a scan rate of 0.05 Vs<sup>-1</sup> using Pt, SnS| PTFE| Pt electrodes. (B) Effect of CO<sub>2</sub> concentration on its reduction profiles in 0.1 M imidazole recorded using SnS| PTFE| Pt electrode at a scan rate of 0.050 Vs<sup>-1</sup>.

Next, CVs were recorded using the SnS| PTFE| Pt electrode for different concentrations of CO<sub>2</sub> as shown in **Figure 6(B)**. It is evident from the figure that the successive rise in CO<sub>2</sub> concentration caused a relative increase in the peak current density ( $j_p$ ) along with a progressive drift of peak potential which can be trait back as a typical feature of an irreversible electron transfer cycle.<sup>46</sup> The typical characteristics of the CVs regarding  $E_i$ ,  $E_p$ , and  $j_p$  observed due to increased concentration ensures that the SnS| PTFE| Pt electrode was stable and reproducible towards CO<sub>2</sub>RR.



**Figure 7.** CVs of CO<sub>2</sub> saturated 0.1 M imidazole solution obtained at a scan rate of 0.05 Vs<sup>-1</sup> using SnS| PTFE| GCE, SnS| PTFE| Au, SnS| PTFE| Graphite, and SnS| PTFE| Pd electrodes.

Further investigation of the performance of the SnS| PTFE catalyst was conducted by immobilizing it onto commonly used electrode surfaces such as GCE, Au, graphite, and Pd. However, as demonstrated in **Figure 7**, the CVs obtained from these electrodes did not exhibit well-defined diffusive voltammograms pertinent to CO<sub>2</sub>RR. Although comparatively higher catalytic currents were observed for graphite and Pd, the kinetic current obtained for bare Pt in **Figure 6(A)** was still significantly higher. Consequently, Pt was deemed the most suitable substrate to further extend the catalytic performance of the novel SnS| PTFE catalyst. Moreover, given that only the SnS| PTFE modified Pt electrode demonstrated outstanding CO<sub>2</sub>RR activity compared to the other modified electrodes, it is reasonable to infer that the CO<sub>2</sub>RR observed on the proposed electrode is attributable to synergistic effects between Pt and SnS| PTFE. Since the SnS| PTFE| Pt electrode displayed promising performance towards CO<sub>2</sub>RR, and thus further studies were carried out using this electrode exclusively. It is important to highlight that, to the best of our knowledge, no prior literature has studied the peak-associated kinetics related to CO<sub>2</sub>RR. Furthermore, we have achieved one of the lowest peak potentials in a well-defined diffusive CV, indicating that the electrode's behavior is activation-controlled for CO<sub>2</sub>RR and is conducive to investigate peak related kinetics.<sup>47,48</sup> While numerous studies have been conducted on electrochemical CO<sub>2</sub> reduction,<sup>17,49</sup> only a few have managed to achieve a diffusive nature of the CV in relation to CO<sub>2</sub> reduction. **Table 1** provides a comparison of various parameters between our study and several previously reported well-defined CV studies.

**Table 1** A comparison of various CV parameter for different electrodes.

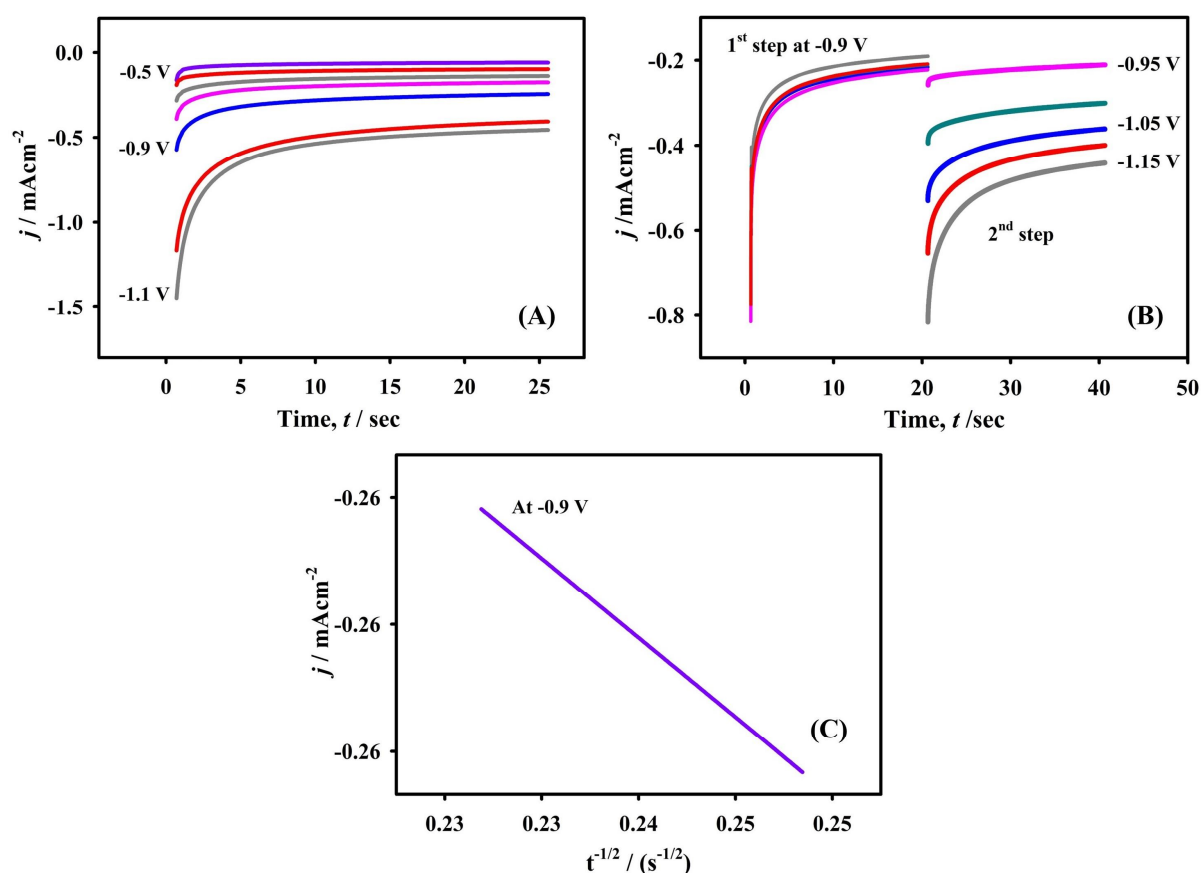
| Electrodes                                                                     | <i>-E<sub>p</sub>/V vs.</i> |                                         |                          | Solvent                                                         | [CO <sub>2</sub> ]/mM | Ref.                 |
|--------------------------------------------------------------------------------|-----------------------------|-----------------------------------------|--------------------------|-----------------------------------------------------------------|-----------------------|----------------------|
|                                                                                | Ag/AgCl<br>(sat. KCl)       | <i>-J<sub>p</sub>/mAcm<sup>-2</sup></i> | <i>v/Vs<sup>-1</sup></i> |                                                                 |                       |                      |
| Ag                                                                             | 2.05                        | 0.1                                     | 0.5                      | [BMIM]TFSI]                                                     | 45                    | 50                   |
| Cu                                                                             | 2.6                         | -                                       | 0.1                      | BMP TFSI                                                        | 454                   | 51                   |
| GCE                                                                            | 2.27                        | 0.25                                    | 0.01                     | BMP TFSI                                                        | 5                     | 52                   |
| [(Mn(TPP)Cl)]/VCE                                                              | 1.4                         | 6                                       | 0.1                      | Acetonitrile                                                    | 230                   | 53                   |
| [Re(BPEBP)(CO) <sub>3</sub> Cl]/Pt                                             | 1.7                         | 2.6                                     | 0.1                      | Acetonitrile                                                    | 280                   | 54                   |
| Co(TPP)Cl/VCE                                                                  | 1.55                        | 0.0176                                  | 0.1                      | [Bu <sub>4</sub> N][BF <sub>4</sub> ]-<br>Acetonitrile +<br>DMF | -                     | 55                   |
| [Co <sup>II</sup> (bipy) <sub>3</sub> ](BF <sub>4</sub> ) <sub>2</sub><br>/GCE | 1.98                        | 0.38                                    | 0.1                      | TBAPF <sub>6</sub> +<br>Acetonitrile                            | -                     | 56                   |
| SnS  PTFE  Pt                                                                  | 1.1                         | 1.52                                    | 0.05                     | Imidazole                                                       | 18                    | <b>This<br/>Work</b> |

$E_p$ : Peak Potential;  $J_p$ : Peak Current Density;  $v$ : Scan Rate; **[BMIM]TFSI**: 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)-imide; **[(Mn(TPP)Cl)]**: 5,10,15,20-tetraphenyl-21H, 23H-porphine manganese(III) chloride; **VCE**: Vitreous Carbon Electrode; **[Re(BPEBP)(CO)<sub>3</sub>Cl]**: fac-(5,5'-bisphenylethynyl-2,2'-bipyridyl)Re(CO)<sub>3</sub>Cl; **BMP TFSI**: 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulphonyl)imide; **Co(TPP)Cl**: cobalt(III)tetraphenylporphyrin; **bipy**: 2,2'-Bipyridine; **[Bu<sub>4</sub>N][BF<sub>4</sub>]**: Tetrabutylammonium tetrafluoroborate; **DMF**: Dimethylformamide; **TBAPF<sub>6</sub>**: Tetra-n-butylammonium hexafluorophosphate; **PTFE**: Poly-tetrafluoroethylene.

### 3.3. Kinetics

#### 3.3.1. Electron Transfer Study

It is demonstrated in the preceding section that CV scanning from -0.2 V to -1.4 V of a solution containing CO<sub>2</sub> (in 0.1 M imidazole) generates a diffusive wave of reduction at -1.1 V vs. Ag/AgCl (saturated KCl) reference electrode referring to CO<sub>2</sub>RR as shown in **Figure 6**. To determine the number of electron transfer and specify the number of steps involved in this Faradaic reduction reaction, chronoamperometric study was carried out both in single step and double step modes by using SnS| PTFE| Pt in 0.1 M imidazole saturated with CO<sub>2</sub>.



**Figure 8.** (A) Single step Chronoamperograms recorded for CO<sub>2</sub> saturated 0.1 M imidazole by using SnS| PTFE| Pt electrode at a potential range of -0.5 to -1.1 V vs. Ag/AgCl (saturated

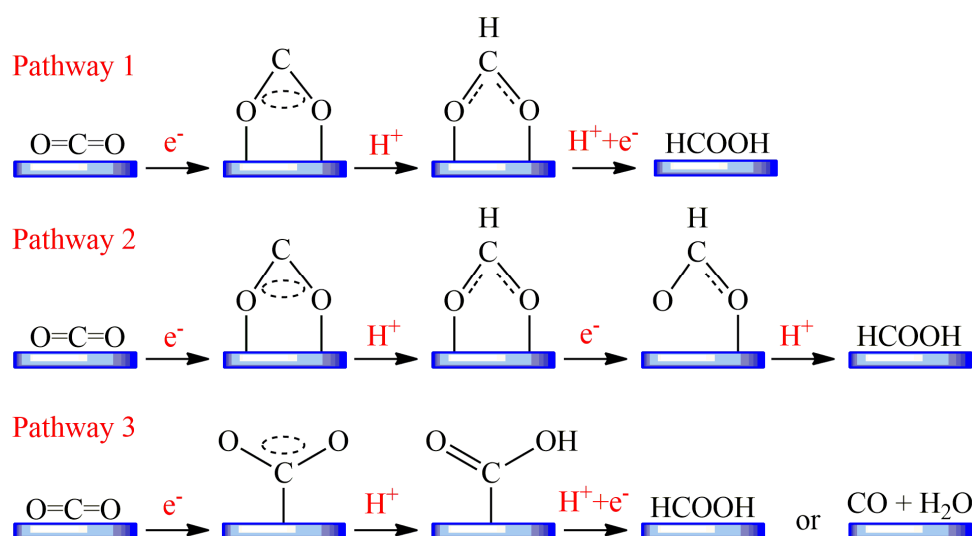
KCl) with an interval of 0.1 V. **(B)** Double step chronoamperograms for CO<sub>2</sub> saturated 0.1 M imidazole by using SnS| PTFE| Pt electrode at a potential range of -0.95 to -1.15 V with the 1<sup>st</sup> step potential kept constant at -0.9 V. **(C)** Displays the linear relationship between diffusional current and inverse of square root of time at potential -0.9 V.

In the single-step mode, a broad spectrum of potentials ranging from -0.5 V was sequentially increased to -0.6, -0.7, -0.8, -0.9, -1.0, and -1.1 V during the recording of chronoamperograms. A sudden exponential increase in reduction current was observed at -0.9 V (**Figure 8A**), suggesting that electron transfers likely occurred at this potential.<sup>57</sup> To investigate the number of steps involved in the electron transfer process, a second step chronoamperometry experiment was performed, with the first step being held constant at -0.9 V. The results of this experiment are shown in **Figure 8(B)**. However, no substantial change in current for the second step was observed which may account for the involvement of multiple step electron transfer process in the reduction reaction.<sup>57</sup> In addition, the exponential decay of current density at -0.9 V with time entails that CO<sub>2</sub> reduction on SnS| PTFE| Pt electrode follows first order kinetics (**Figure 8B**). Consistently, the  $j$  vs.  $t^{1/2}$  relationships, obtained in any potential between -0.9 V and -1.1 V, exhibited excellent agreement with the well-known Cottrell equation, expressed as equation(1).<sup>57</sup>

$$j = \frac{nFC\sqrt{D}}{\sqrt{(\pi t)}} \quad (1)$$

Where,  $j$  represents current density (Acm<sup>-2</sup>),  $n$  denotes electron number,  $C$  stands for concentration of analyte (mol.cm<sup>-3</sup>),  $D$  is the diffusion coefficient expressed as  $1.7 \times 10^{-5}$  cm<sup>2</sup>s<sup>-1</sup> for CO<sub>2</sub>,<sup>58</sup>  $t$  = time (s).

The slope value of the  $j$  vs  $t^{1/2}$  plot acquired at -0.9 V (**Figure 8C**) was harnessed to quantify the number of electrons involved in the CO<sub>2</sub>RR using equation (1), which was calculated to be 1.86 ( $\approx 2$ ). The slope value suggests that a  $2e^-$  transfer pathway was associated with the CO<sub>2</sub>RR. The proposed reaction pathways corresponding to a  $2e^-$  transfer CO<sub>2</sub> reduction reaction are presented as **Scheme 1**.

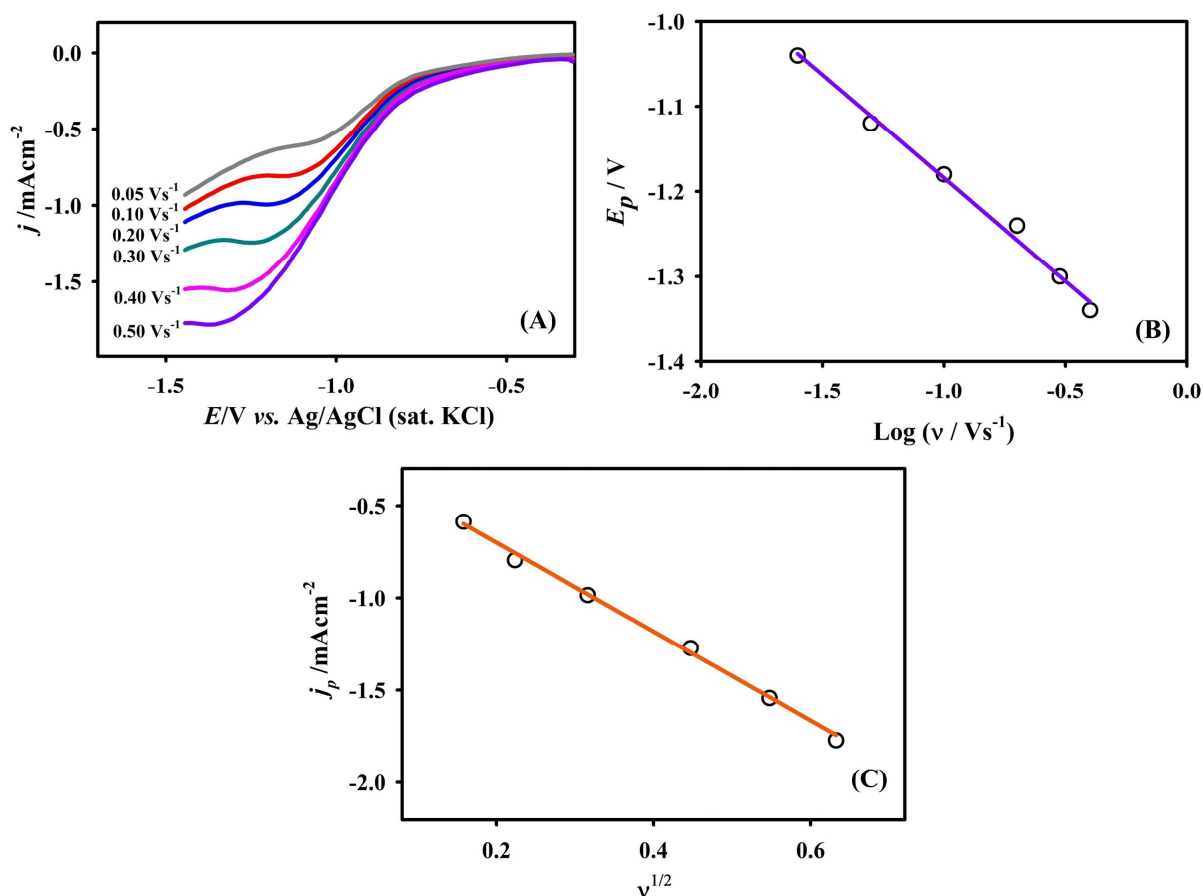


**Scheme 1.** Probable CO<sub>2</sub> reduction pathways on SnS| PTFE| Pt electrocatalytic surface.<sup>35</sup>

Production of formate and CO follows these three pathways illustrated in **Scheme 1**. However, the product selectivity largely depends on whether the first proton coupling occurs on the carbon or the oxygen atom of the adsorbed CO<sub>2</sub> radical anion.<sup>59</sup> If the protonation takes place on the carbon atom, then it forms an HCOO<sup>•</sup> intermediate. Afterwards, a second electron transfer and protonation lead to the formation HCOOH product, which is illustrated as the pathway 1. But unlike pathway 1, an extra step is involved in pathway 2 where an electron transfer converts the HCOO<sup>•</sup> to a <sup>•</sup>OCHO intermediate. In this route, HCOOH formation occurs via the protonation of the <sup>•</sup>OCHO intermediate. Finally, in pathway 3, protonation of the oxygen atom in CO<sub>2</sub> radical anion leads to the formation of the <sup>•</sup>COOH intermediate. After that the second electron transfer and protonation lead to the reduction of the intermediate to produce either HCOOH or CO by losing water. Systematic electrochemical investigations were conducted and discussed in the subsequent sections to explore the kinetics involved in CO<sub>2</sub> reduction reaction and to unveil the most probable reaction product.

The interrelation between the current-potential relationship in voltammetry and scan rate often enables the acquisition of crucial kinetic information about an electrochemical reaction. Therefore, linear sweep voltammograms (LSVs) were obtained by varying scan rate from 0.05 to 0.5 Vs<sup>-1</sup> for CO<sub>2</sub> saturated 0.1 M imidazole solution. The corresponding analysis demonstrates that the peak current ( $j_p$ ) of the reduction profile increased progressively with the sequential increase in sweep rate, as depicted in **Figure 9(A)**. The observed elevation in peak potential ( $E_p$ ) with increasing scan rate (**Figure 9B**) indicates the predominantly irreversible

nature of the electrode process, and the linear  $j_p$  vs  $v^{1/2}$  relationship (**Figure 9C**) indicates that CO<sub>2</sub>RR was driven by diffusion.<sup>60</sup> The difference between the peak potential ( $E_p$ ) and half-peak potential ( $E_{p/2}$ ) was observed within the range of 23 to 28 mV. The slope of the  $E_p$  vs  $\log(v)$  plot was found to be -23.9 mV (**Figure 9B**). This result indicates that electron transfer dominated the reduction reaction rate on the SnS| PTFE| Pt surface in 0.1 M imidazole. **Figure 9(B)** further demonstrates that peak potential shifts to more negative values as the scan rate is increased. This can be attributed to the fact that thickness of the diffusion layer decreases with the increment of scan rate. The shorter diffusion path enables more CO<sub>2</sub> molecules to reach the active electrode surface resulting in the requirement of elevated potential to conduct CO<sub>2</sub>RR.<sup>60</sup> Subsequently, for the characterization of the electron transfer process, the transfer coefficient ( $\alpha$ ) was determined by evaluating the dependence of  $E_p$  and  $E_p - E_{p/2}$  on scan rate from equation (2) and equation (3), respectively.<sup>61</sup>

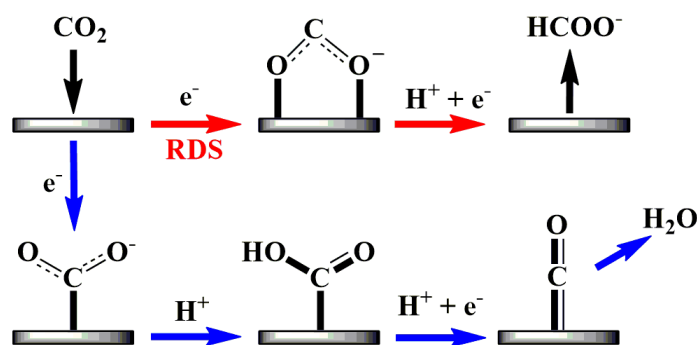


**Figure 9.** (A) Linear sweep voltammograms (LSVs) acquired for CO<sub>2</sub> saturated 0.1 M imidazole solution, demonstrating a dependence on the scan rate. (B) The correlation between the peak potential ( $E_p$ ) and the natural logarithm of scan rate,  $\ln(v)$ . (C) Relationship between the peak current ( $j_p$ ) and square root of scan rate ( $v^{1/2}$ ).

$$\alpha = \frac{-RT}{F (\partial E_p / \partial \log v)} \quad (2)$$

$$\alpha = \frac{1.86 RT}{F |E_p - E_{p/2}|} \quad (3)$$

Using equation (2) and (3), the value of  $\alpha$  was determined to fall within the range of 0.17 to 0.21, across varying scan rate of 0.05 to 0.5  $\text{Vs}^{-1}$ . An  $\alpha$  value less than 0.5 indicates the presence of a slow step, in which radical species ( $\text{COO}^{\bullet-}$ ) are formed, following the initial electron transfer.<sup>62</sup> This further implies that a two-step electrode process was involved, with the initial step being rate-determining, followed by a faster heterogeneous electron transfer step. The rate of radical anion formation on the catalytic surface was slower compared to the rate of the second electron transfer step.<sup>63</sup> The first electron transfer step becoming the rate determining step (RDS) in  $\text{CO}_2\text{RR}$  on the developed  $\text{SnS| PTFE}$  modified Pt electrode strongly suggests the formation of formate anion via an overall two electron transfer step as shown by the red arrows in **Scheme 2**.<sup>64</sup>



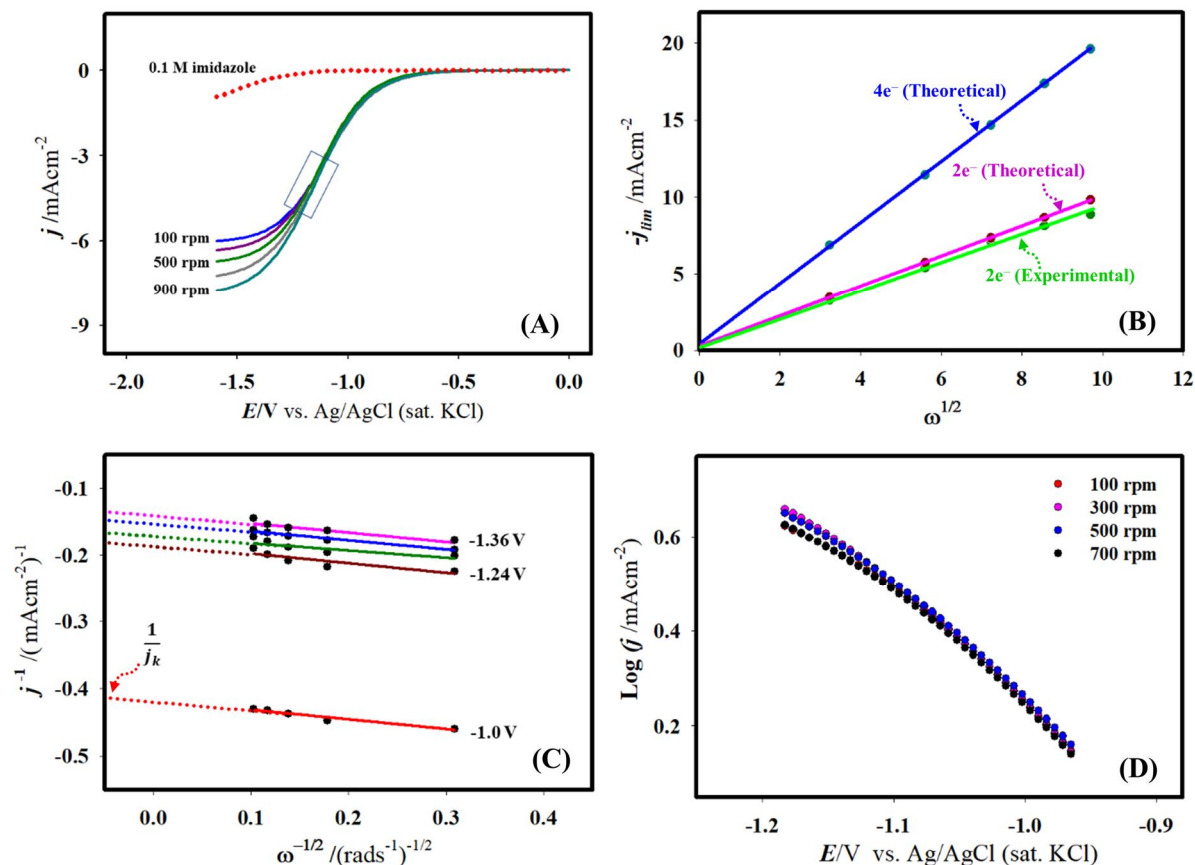
**Scheme 2.** The two possible pathways involving a radical anion intermediate in the electrocatalytic reduction of  $\text{CO}_2$ . Pathway from  $\text{CO}_2$  to  $\text{HCOO}^-$  is indicated by red arrows and from  $\text{CO}_2$  to  $\text{CO}$  by blue arrows.

According to the transfer coefficient study, the electrochemical reduction of  $\text{CO}_2$  occurred via a two-electron transfer mechanism involving an RDS as opposed to having both steps follow a fast electron transfer kinetics, which would ultimately result in the production of  $\text{CO}$  by losing water.

### 3.3.2. Hydrodynamic Voltammetry Analysis

It was stated in the preceding section that the magnitude of transfer coefficient ( $\alpha$ ) stayed nearly constant regardless of the applied scan rate for achieving  $\text{CO}_2\text{RR}$ . The observed constancy of  $\alpha$  implies that the Butler-Volmer model of kinetics is compatible in the current

case.<sup>62,65</sup> Hence, the rotating disk electrode (RDE) analysis was carried out to analyze the kinetics of CO<sub>2</sub>RR. **Figure 10(A)** displays the hydrodynamic voltammograms obtained by altering electrode rotation rate from 100 to 900 rpm, using a fixed scan rate of 0.05 Vs<sup>-1</sup> with CO<sub>2</sub> saturated 0.1 M imidazole solution.



**Figure 10.** (A) Hydrodynamic voltammograms of CO<sub>2</sub> saturated 0.1 M imidazole solution recorded using the SnS| PTFE| Pt electrode (area: 0.042 cm<sup>2</sup>). These data were taken at varying electrode rotation rates in the range of 100-900 rpm at 0.05 Vs<sup>-1</sup>. (B) Levich plots generated to analyze various electron transfer processes. (C) Koutecky-Levich (K-L) plots constructed at different potentials, and (D) Tafel plots derived from Figure 10(A) at different rotations rates.

Similar to CV measurements, CO<sub>2</sub> reduction in hydrodynamic voltammograms started at potentials lower than OCP value shown in **Figure 4**. Moreover, the limiting current ( $j_l$ ) was observed to elevate progressively at increased rotation rates. It was noted from **Figure 10(A)** that the limiting current ( $j_l$ ) initiated at -1.1 V vs. Ag/AgCl (saturated KCl) at 100 rpm and shifted towards more positive potentials with each subsequent increase in rotation rates. The limiting current ( $j_l$ ) for CO<sub>2</sub>RR can be defined by equation (4) which is commonly known as the Levich equation.<sup>66,67</sup>

$$j_l = 0.62nFC_bD_o^{2/3}\nu^{-1/6}\omega^{1/2} \quad (4)$$

Where ‘n’ represents the number of electrons involved in the reduction reaction, F denotes the Faraday constant (96,500 C),  $C_b$  represents the bulk concentration of  $\text{CO}_2$  ( $2 \times 10^{-3} \text{ mol cm}^{-3}$ ),  $D_o$  signifies the diffusion coefficient of  $\text{CO}_2$  ( $1.71 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ),<sup>58</sup>  $\nu$  indicates the viscosity of the medium, and  $\omega$  corresponds to the angular rotation which is defined as  $\omega = 2\pi f/60$ , where  $f$  denotes the rotation per minute (rpm).

The estimated number of electrons transfer involved in  $\text{CO}_2\text{RR}$  was calculated by extracting the values of  $j_l$  from **Figure 10(A)**. Utilizing equation (4), a linear relationship between  $j_l$  and  $\omega^{1/2}$ , with a slope equal to  $0.62nFC_bD_o^{2/3}\nu^{-1/6}$  was obtained, where the slope value incorporates the number of electrons transferred (n) during  $\text{CO}_2$  reduction. The solid line in **Figure 10(B)** constructed using experimental  $j_l$  data plotted against  $\omega^{1/2}$ , exhibited a straight line having a slope value of  $0.92 \text{ mAcm}^{-2} (\text{rad s}^{-1})^{-1/2}$ . Next, theoretical Levich lines represented by blue and pink lines in **Figure 10(B)** were estimated for  $n = 4$  and  $2$ , respectively. The slope values for  $n = 2$  and  $n = 4$  were determined to be  $0.98 \text{ mAcm}^{-2} (\text{rad s}^{-1})^{-1/2}$  and  $1.98 \text{ mAcm}^{-2} (\text{rad s}^{-1})^{-1/2}$ , respectively. The agreement between the experimentally determined slope value of  $0.92 \text{ mAcm}^{-2} (\text{rad s}^{-1})^{-1/2}$  and the theoretical slope calculated for  $n = 2$  confirms that the  $\text{CO}_2\text{RR}$  involved a  $2e^-$  transfer process based on the principle of equation (4).

Koutecky-Levich (*K-L*) plot analysis is a comprehensive technique employed for evaluating the kinetics of an electrochemical reaction. In the present study, *K-L* linear model was utilized to gain insights into the relevant kinetics and determine the kinetic order, as defined by equation (5).<sup>68</sup>

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{0.62 nFC_bD^{2/3}\nu^{-1/6}\omega^{1/2}} \quad (5)$$

Where,  $j_k (= nFCk^o)$  represents the kinetic limited current at the infinite rotation, and  $k^o$  signifies the heterogenous rate constant. According to the equation (5), the  $j^{-1}$  vs.  $\omega^{-1/2}$  plots should exhibit linear relationships with an intercept corresponding to  $1/j_k$ . The slopes ( $0.62 nFC_bD^{2/3}\nu^{-1/6}$ ) of the straight lines involves the number of the electrons participating in the irreversible reaction. By extracting the  $j^{-1}$  values from **Figure 10(A)** at various potentials and plotting them as a function of  $\omega^{-1/2}$ , *K-L* plots were constructed. The *K-L* lines acquired at different potentials within the diffusional zone are displayed in **Figure 10(C)**. The presence of linear parallel lines indicate that the reduction reaction followed first-order kinetics on the

surface of the SnS| PTFE| Pt electrode implying that the rate of CO<sub>2</sub>RR was directly proportional to the concentration of CO<sub>2</sub> in the bulk of the imidazole solution. By analyzing the slopes of the *K-L* plots obtained between the voltage range of -1.24 to -1.36 V vs. Ag/AgCl (saturated KCl), the number of electron transfer was determined using equation (5) to be  $1.87 \pm 0.05$ . This observation provides further validation for the involvement of a 2e<sup>-</sup> transfer reaction during the reduction process at the SnS| PTFE| Pt surface.

The linear Tafel equation (6) can be employed effectively to extract various additional kinetic parameters from *j* vs. *E* plots obtained from hydrodynamic voltammetry experiments at different rotation rates.<sup>69,70</sup>

$$\log(j) = \log(j_k) + b(E - E^{\circ'}) \quad (6)$$

Where  $E^{\circ}$  represents the formal potential, *E* is the applied potential vs. Ag/AgCl (saturated KCl),  $b = \frac{2.3.03RT}{\alpha F}$  is the Tafel slope and  $j_k (= nFck^{\circ})$  represents the exchange current at  $E = E^{\circ'}$ . Analysis of **Figure 10(A)** reveals that within a narrow potential range of -1.1 to -1.3 V (indicated by a parallelogram), the currents values are independent of electrode rotation, indicating that in this potential range, the currents intensity is primarily controlled by the electron transfer kinetics. In this potential window, the electron-transfer rate at the electrode surface is significantly lower than the diffusion-convection limiting rate (i.e.,  $j_d \gg j_k$ ), leading to the current intensity being almost equal to  $j_k$ . The current intensities within this limited potential range were employed to derive the exchange current intensity at infinite rotation, which was then utilized to compute the standard potential of CO<sub>2</sub> reduction process using the Tafel equation (6).

**Figure 10(D)** displays the log (*j*) vs *E* plot for three different rotations. The intercept of **Figure 10(C)** shows that at a potential -1.0 V vs. Ag/AgCl (saturated KCl),  $j_k$  corresponds to a value of 2.5 mAcm<sup>-2</sup>, indicating a  $k^{\circ}$  value of  $1.7 \times 10^{-6}$  cms<sup>-1</sup>. By substituting the value of kinetic controlled exchange current ( $j_k$ ) into the intercept of linear Tafel plots at various rotations, the value of  $E^{\circ'}$  was determined to be -0.15 V from equation (6), which aligns with the OCP value shown in **Figure 4**. The average transfer coefficient ( $\alpha$ ), calculated from the Tafel slope values, was found to be 0.22, which is consistent with the results obtained from steady state voltammetry as shown in the earlier section (3.3.1.). This implies a consecutive transfer of two electrons from the analyte to the electrode, with the involvement of a slower

electron transfer step (RDS),<sup>62</sup> as illustrated by the reduction route indicated by the red arrow in **Scheme 2**.

### 3.4. Product Analysis

To validate the generation of the formate compound via  $2e^-$  transfer kinetics discussed so far, a GC-MS instrument was utilized. The GC-MS analysis involved subjecting a  $CO_2$ -saturated imidazole solution to bulk electrolysis using the SnS| PTFE| Pt electrode at -1.1 V vs. Ag/AgCl (saturated KCl) for a duration of 1 hour. **Figure S1(A)** in the Supporting Information illustrates the gas chromatogram of the solution subsequent to bulk electrolysis. The distinct peak observed at a retention time of 1.18 min indicates the presence of  $CO_2$ , while the peak at 2.0 min confirms the formation of formate during  $CO_2$  electrolysis. **Figure S1(B)** showcases the mass spectrum of the formate compound generated during electrolysis process.

## 4. Conclusion

Sn based electrocatalyst modified with sulfur were studied for  $CO_2$  reduction reaction in alkaline imidazole medium. Polymer supported SnS nanomaterials were successfully immobilized on the Pt surface. From the voltametric kinetic study, it was deduced that the catalyst selectively produce formate at moderate overpotential. Transfer coefficient ( $\alpha$ ) study indicated the involvement of an RDS among the two-step electron transfer kinetics that served as a proof for the production of formate over CO during  $CO_2$  reduction on the SnS| PTFE| Pt electrode. GC-MS analysis confirmed the production of formate compound in bulk electrolysis process. Scan rate dependent LSV analysis revealed that the reaction was diffusion-controlled, whereas the RDE study showcased the first order kinetics of  $CO_2$ RR. Overall, these findings provide us a new dimension for SnS based energy materials for  $CO_2$  reduction reaction, thus offering numerous valuable insights for further understanding of  $CO_2$  reduction kinetics towards formate production.

### Authors' Contribution

**Md. Tarikul Islam:** Experimental, Data analysis, Writing original draft; **Mohammad Imran Hossain:** Experimental, Writing- original draft, review & editing, Preparing figures; **Kentaro Aoki:** Characterization; **Yuki Nagao:** Characterization; **Md. Mahmudul Hasan:** Characterization; **Mostafizur Rahaman:** Funding acquisition, Writing- review & editing; **Ali**

**Aldalbahi:** Funding acquisition, Writing- review & editing; **Mohammad A. Hasnat:** Funding acquisition, Conceptualization, Overall supervision.

### Supporting Information

Structural parameters of SnS crystal, gas chromatograph of CO<sub>2</sub> saturated 0.1 M imidazole solution after 1 hour of bulk electrolysis, and mass spectrum of the formate compound produced during electrolysis.

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